

# Intrinsic Doping at YBCO-metal Interfaces: Quantitative Results

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**Abstract.** – Charge redistribution in high- $T_c$  superconductors due to structural defects or interfaces is known to be crucial for electronic applications as the band structure is modified on a local scale. In order to investigate these effects in more detail, we address the normal-state properties of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (YBCO) in the vicinity of YBCO-metal interfaces by electronic structure calculations for well relaxed interface configurations. Our findings can be interpreted in terms of a band-bending mechanism complemented by local screening effects. We derive quantitative results for the intrinsic doping of the superconducting  $\text{CuO}_2$  planes due to the metal interface. In particular, the net charge transfer amounts to 0.13 electrons in favour of each intraplane copper site, which appears to be a typical value for interfaces of high- $T_c$  superconductors, thus opening great possibilities for a systematic optimization of wires and tapes from high- $T_c$  materials.

*Introduction.* – High- $T_c$  superconductors differ strikingly from conventional superconductors with respect to transport properties at interfaces and grain boundaries. For example, low values of critical current densities pose severe problems for large-current applications [1]. For  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , enhancement of the transport is reached by local calcium overdoping [2, 3]. This effect is connected to phenomena such as interface charging and modifications of the local electronic band structure, which can be modelled via the charge redistribution at superconductor-metal interfaces. In general, a large variety of technical applications of such interfaces makes insight into the details of the local electronic structure highly desirable.

Bending of the band structure as induced by local variations of the charge distribution in high- $T_c$  materials is strong enough to control the superconducting properties [4, 5] due to large dielectric constants and small carrier densities, characteristic for high- $T_c$  materials [6]. As a consequence, the Thomas-Fermi screening length, over which band-bending is effective, reaches up to more than 1 nm and therefore is comparable to the superconducting coherence length. For  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , experimental evidence that grain boundaries are depleted of charge carriers comes from electron energy loss spectroscopy [7, 8].

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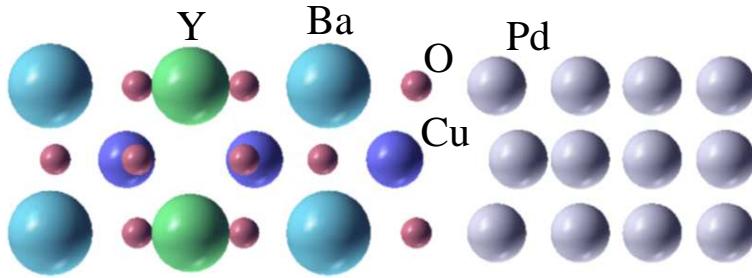


Fig. 1 – YBCO-metal interface as resulting from the structure optimization when the Pd sites are assumed to be placed on top of the interface O sites (configuration A)

From the theoretical point of view, formation energies required for substituting dopants on different YBCO lattice sites and oxygen vacancy formation energies have been addressed by Klie *et al.* [9]. Their first-principles calculations indicate oxygen deficiency and consequently hole depletion at undoped grain boundaries, which both are removed by calcium doping. Effects of charge modulation at the surface of high- $T_c$  superconductors have been studied by Emig *et al.* [10], who found that surfaces are covered by dipole layers, due to a local suppression of the gap function. In addition, the charge imbalance arising at the boundary between a short coherence length superconductor and a normal metal has been studied by Nikolic *et al.* [11] in the framework of a self-consistent microscopic approach.

The technical optimization of interfaces of high- $T_c$  superconductors calls for knowledge about the local band-bending magnitude at the different atomic sites, which we address in the following. Since the local electronic structure in the vicinity of interfaces strongly depends on the local atomic configuration, it is necessary to start from the details of the crystal structure in order to obtain quantitative results. Probably due to their high demand on CPU time, state-of-the-art electronic structure calculations meeting this requirement are still missing. In this letter we present first-principles calculations for YBCO-metal interfaces, based on density functional theory and the generalized gradient approximation as implemented in the WIEN2k program package, a full-potential linearized augmented-plane-wave code [12]. Apparently for the first time, we derive quantitative results for the intrinsic doping of the superconducting  $\text{CuO}_2$  planes induced by the metal interface.

*Structural Considerations.* – Since band-bending is proposed to take place on the length scale of the YBCO lattice constant, the electronic properties of YBCO-metal interfaces become accessible to a supercell approach with periodic boundary conditions. Our subsequent calculations are based on supercells along the crystallographical  $c$ -axis, whereas possible  $ab$ -superstructures are not taken into account for reasons of calculational complexity. The latter is justified for moderate lattice mismatch. To be more specific, we use the YBCO  $ab$ -lattice constants to set up our supercells, thus  $a = 3.865 \text{ \AA}$  and  $b = 3.879 \text{ \AA}$  [13]. In order to minimize forces, the atomic coordinates of the experimental YBCO structure are optimized in a first step [14, 15]. The structural relaxation of the supercells then starts from these data, where convergence is assumed when the boundary forces have decayed.

As metallic substituent we choose fcc palladium due to a minimal lattice mismatch ( $c_{\text{fcc}} = 3.89 \text{ \AA}$ ) of about 0.7%. Along the  $c$ -axis, our supercells consist of 2 YBCO unit cells, terminated by the CuO-chain layers [16–18], and 4 metallic unit cells in an [001] orientation. The resulting supercell therefore belongs to space group Pmm2, comprising 46 inequivalent atomic sites. As starting point of the structural relaxation, there are two natural interface

	Configuration A	Configuration B
$d_{\text{Cu-Pd}}$	3.32 Å, 3.79 Å	2.68 Å, 3.81 Å
$d_{\text{O-Pd}}$	2.12 Å, 3.87 Å	2.70 Å, 2.72 Å
$d_{\text{Cu-O}}$	2.02 Å	2.08 Å
$d_{\text{Cu-O}_{\text{Ba}}}$	1.90 Å	1.81 Å

TABLE I – *Bond lengths close to the YBCO-metal interface as resulting from the structure optimization.*

configurations where the metallic sites are placed on top of the interface oxygen (configuration A) or copper (configuration B) sites, respectively. Since we found that our conclusions about the band-bending mechanism do not depend on the configuration used, the following considerations focus on configuration A. As far as these results are concerned, *ab*-superstructures thus likewise seem to play a minor role.

The structure optimization of our supercells shows a strong tendency towards Pd-O bonding at the interface. In addition, significant repulsion of copper and palladium is observed. In the metal region, the structural relaxation affects almost exclusively the first atomic layer, whereas in the YBCO region mainly the CuO-chain layer as well as the BaO layer are involved. The O sites of the interface CuO-chain are shifted out of plane. In configuration A, a strong buckling of the first Pd layer allows the system to avoid Cu-Pd overlap, whereas this buckling is considerably reduced in configuration B. The supercell of configuration A as resulting from the structure optimization is depicted in Fig. 1 in a projection along the *a*-axis, thus perpendicular to the CuO-chains. Corresponding bond lengths are summarized in Tab. I. While the bond lengths in the Cu-O chain of bulk YBCO amount to 1.94 Å, the values 2.02 Å and 2.08 Å are found for interfaces A and B, respectively. Moreover, we observe a reduced bond length of 1.81 Å between the chain Cu sites and the neighbouring O sites in the BaO layer of configuration B, whereas in configuration A the bulk value of 1.90 Å persists.

*Results.* – In the following, band structure data for bulk YBCO, without interface, will act as a reference for the interpretation of the data. We mention that our bulk YCBO band structure agrees well with previous calculations using the local density approximation and likewise reveals good agreement with experimental observations, see [19–21] and the references given therein.

For the YBCO-metal interface, we first investigate the palladium sites. Fig. 2 displays partial Pd 4*d* densities of states for the sites in the 1st and 3rd metal layer. Here and in the following, layers are counted with respect to the interface, i.e. the 1st metal layer is attached to the CuO-chains of the YBCO cell. For comparison, we include a fcc bulk Pd DOS in Fig. 2. While for the 1st and 2nd metal layer Pd states are shifted from the Fermi level both to higher and lower energies, the local DOS for sites in the 3rd and further layers almost resembles the bulk DOS. Hence the electronic screening length is found to be small in the palladium region, as expected.

Turning to the YBCO region, we first address the CuO-chain layers, for which Cu 3*d* densities of states are shown in the upper panel of Fig. 3. Because of Cu-O bonding, copper and oxygen states give rise to a broad structure in the energy region from about −6.5 eV to 1.5 eV, with respect to the Fermi level. While the 1st chain layer is affected by strong modifications of the electronic bands due to structural relaxations at the interface, the Cu sites in the 2nd chain layer (one YBCO unit cell off the interface) are found to resemble the electronic structure of the respective bulk YBCO Cu sites, see Fig. 3. However, we note that the bulk DOS is shifted to lower energies by 0.3 eV in order to reconcile the curves. As the

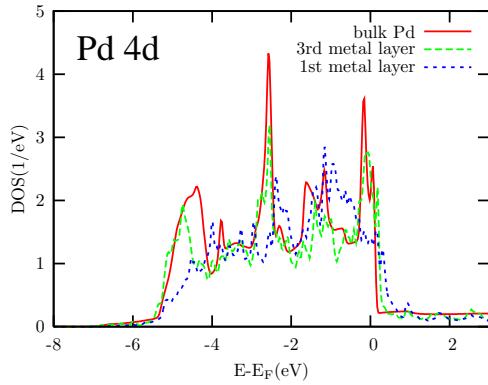


Fig. 2 – Partial Pd 4d DOS for metal layers parallel to the YBCO-metal interface. With increasing distance to the interface the curves quickly converge to the bulk Pd DOS.

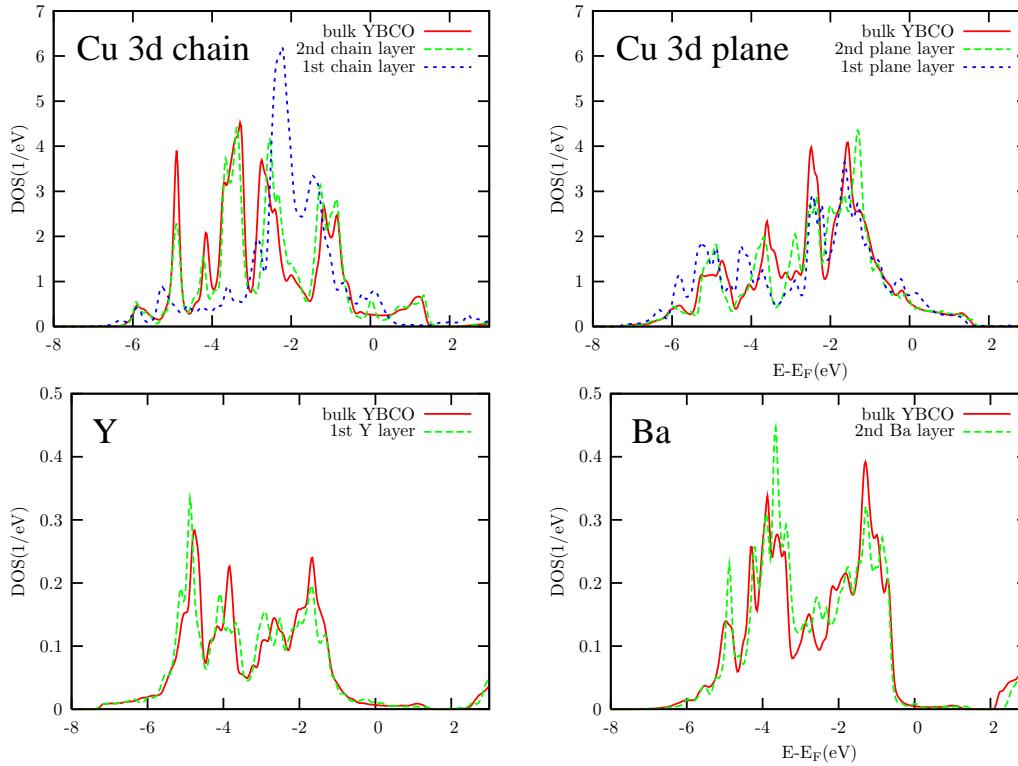


Fig. 3 – Partial Cu 3d (CuO-chain and CuO<sub>2</sub>-plane sites), Y and Ba DOS. The second CuO-chain layer resembles the bulk YBCO Cu DOS when the latter is shifted by 0.3 eV to lower energies. Similar energetical shifts of 0.3 eV and 0.45 eV are found for the Y and Ba sites, respectively. The second CuO<sub>2</sub>-plane resembles the bulk YBCO Cu DOS in the vicinity of the Fermi level when the latter is shifted by 0.2 eV to lower energies, which corresponds to a reduction of 0.13 holes per Cu site.

fine structure of the 2nd chain layer DOS is hardly affected by the interface, we can interpret this shift in terms of almost ideal down bending of the electronic bands due to a modified Fermi level.

Small contributions of Y and Ba states in the copper dominated energy interval, as shown in the middle and lower panel of Fig. 3, respectively, are a consequence of weak covalent bonding, mainly with oxygen states. Although Y and Ba act as electron donors, in principle, these contributions close to the Fermi level are well suitable for analyzing possible band-bending effects at the cation sites. For the 1st Y and 2nd Ba layer (the 1st Ba layer is affected by structural recombinations) the DOS curves of Fig. 3 show almost perfect agreement with the respective bulk YBCO Y/Ba DOS when adequate energetical shifts are applied. Again, for the Y sites a shift of 0.3 eV is convenient, while a shift of 0.45 eV is necessary for the Ba sites. To understand this fact, effects of electronic screening have to be taken into consideration. Both the Y and Cu chain sites (see the previous discussion) reveal a finite number of electronic states right at the Fermi level, whereas for Ba the DOS almost vanishes. For this reason, screening is less efficient at the Ba sites and band-bending effects become more pronounced. Energetical shifts of core levels at atomic sites near the interface are fully consistent with this interpretation.

The local charge distribution in the CuO<sub>2</sub>-planes near interfaces is of central interest for the YBCO transport properties. In particular, effects of interface charging and modifications of the electronic band structure near grain boundaries, where superconductivity is locally suppressed due to the imperfections of the crystal structure, can be modelled. Partial Cu 3d densities of states for CuO<sub>2</sub>-plane sites in the 1st and 2nd layer off the interface are compared to the corresponding bulk YBCO Cu DOS in Fig. 3. While for the 1st layer some additional Cu states appear around the Fermi energy, which grow out of the modified Cu-O bonding at the interface, the DOS of the 2nd CuO<sub>2</sub>-plane perfectly fits the bulk YBCO Cu DOS shape close to the Fermi level. In contrast to the local band-bending magnitudes at the previously addressed YBCO sites, here an energetical shift of 0.2 eV is found to be sufficient to reconcile the curves. This fact agrees well with the screened band-bending mechanism due to the high charge carrier density in the CuO<sub>2</sub>-planes. As compared to the bulk charge distribution, the 0.2 eV down bending of the Cu 3d bands comes along with a charge carrier depletion of 0.13 holes per Cu site. Importantly, both this value and the calculated band-bending magnitudes seem to be rather general results as similar numbers are found when silver is used as metallic substituent.

Because of an electrostatic screening length of a few nanometers in high-T<sub>c</sub> cuprates and the inhomogeneity of the crystal structure, the conventional band-bending models based on a continuum description of the charge distribution are not applicable. Screening effects result in a significant reduction of the band-bending magnitude and therefore in reduced charge transfer. In particular, the calculated 0.13 hole depletion per Cu site seems to explain the observation that local hole-doping of grain boundaries, via replacing Y by Ca, leads to enhanced supercurrent densities. Schmehl *et al.* [2] find the maximal enhancement for 30% Ca doping, i.e. doping of 0.3 holes per CuO<sub>2</sub> unit. Assuming that doping effects predominantly affect the CuO<sub>2</sub>-planes adjacent to the Y/Ca sites, this value agrees even quantitatively with our band structure result of 0.26 holes. The latter maintains when we take into account that the experimental value relies on oxygen deficient samples, YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub>, since the magnitude of screened band-bending in the CuO<sub>2</sub>-planes is expected to be almost independent of the oxygen content.

Moreover, our findings cast doubts on the role of oxygen deficiency reduction by Ca doping as claimed by Klie *et al.* [9]. The authors attribute the reduction of the local hole depletion at grain boundaries to the removement of intrinsic excess oxygen vacancies, induced by Ca

doping. In contrast, our results indicate that modifications of the oxygen concentration are less important. At least for YBCO-metal interfaces band-bending is sufficient to explain the reported doping effects.

Xu and Ekin report on specific resistivities for YBCO-Au interfaces of  $10^{-4} \Omega \text{cm}^2$  to  $10^{-3} \Omega \text{cm}^2$  at low temperatures [22]. However, our calculations for normal-state YBCO interfaces do not show a significant reduction of the Cu 3d DOS in the vicinity of the Fermi level. Even though no insulating layer is formed at the interface, the screened band-bending mechanism still can explain the observed interface resistivity. Since the charge carriers in the CuO<sub>2</sub>-planes are reduced, the superconductivity is locally disturbed.

*Conclusions.* – We have discussed electronic structure calculations for interfaces between the short coherence length superconductor YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> and the normal metal palladium in order to analyze the influence of the charge redistribution induced by interfaces on the local doping of the superconductor. Based on well relaxed interfaces, we have found that modifications of the charge distribution with respect to the bulk are well screened in the metal region, whereas they affect the superconductor on a nanometer length scale. Specifically, our calculations result in a net charge transfer of about 0.13 electrons in favour of each Cu site in the CuO<sub>2</sub>-planes, in correspondence with the experimental observation of charge carrier depletion.

In particular, our results are consistent with the fact that artificial hole-overdoping of grain boundaries yields significant improvement of the transport properties. The depletion of charge carriers due to the interface is compensated and a state of optimal doping is reached. Our calculations agree even quantitatively with experiment as concerns the amount of hole-overdoping needed for obtaining an optimally doped interface. It turns out that screening strongly affects the magnitude of the charge redistribution in the CuO<sub>2</sub>-planes, which has serious consequences for the design of interface structures, such as S-N-S Josephson contacts, for instance. Expectedly, the mechanism of screened band-bending and the net charge transfer are almost independent of the specific high-T<sub>c</sub> material and metal forming the interface. Therefore our results are very general and can be applied to a large variety of interface configurations, thus paving the way for systematic material optimization.

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